

Domtar

ACID RAIN AND THE FOREST: THE EFFECT OF ALUMINUM AND
THE GERMAN EXPERIENCE. / Tomlinson, G.H. 1981.

CA 7 DT 81A16



Research Memorandum

PROJECT NO. 74-7124-13



Earth Sciences Library

ACID RAIN AND THE FOREST - THE EFFECT OF ALUMINUM
AND THE GERMAN EXPERIENCE



Environmental Studies
University of Toronto
Haultain Building
Toronto, Ontario, Canada
M5S 1A4

G. H. Tomlinson

February 1981

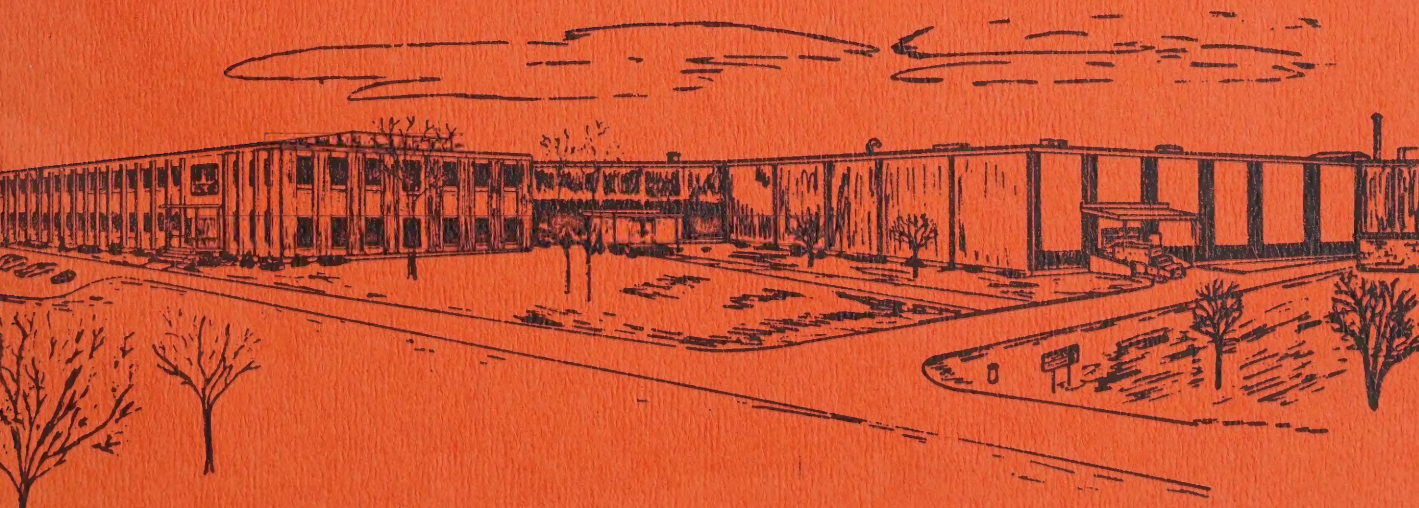


TABLE OF CONTENTS

A. Summary	1
B. Introduction	2
C. Observations Made with Regard to Forest Ecosystems	4
1. The Effect of Forest Canopy on the Input of Sulfur, Hydrogen and Other Ions on the Forest Floor	4
2. The Accumulation of Carbon and Nitrogen in the Humus of the Beech Forest	7
3. The Changes in Soil Chemistry in the Beech Forest and the Resultant Effect on the Forest	7
4. The Effect of an Acidifying Forest Ecosystem and Fluxes and Stores of Nutrients	9
5. The Changes in Soil Chemistry in the Spruce Forest and the Resultant Effect on the Forest	11
6. The Dieback of Silver Fir in Central Europe	12
D. Significance of German Findings for Canada	13

Appendix

1. Soil Reactions Involving a Change in the H^+ Status of Soil Solution	16
2. Increasing Soil Acidity and the Dissolution of Mineral Ions from the Soil	18
3. Ion Take-Up by the Tree Roots	20
4. Methods of Sampling Used in Measurement of Ionic Balances	20
5. The Cation Exchange Capacity	21
6. Appendix Summary	22

Bibliography

Tables

Figures



Digitized by the Internet Archive
in 2025 with funding from
University of Toronto

<https://archive.org/details/31761056886047>

G.H. Tomlinson
February 1981

A. SUMMARY

For the past fifteen years, Dr. Ulrich and his associates at the University of Göttingen have been carrying out detailed studies on the interaction of inputs from the atmosphere, soil characteristics and their effect on forest trees.

They have found that in the principal area under study:

1. The forest foliage and bark capture and oxidize sulfur dioxide present in very low concentration in the atmosphere. The resultant sulfuric acid together with that contained in aerosols, also deposited in the canopy from the atmosphere, are washed from the trees with rain. In the beech forest, as a result, acid reaching the forest floor is annually twice that in the rain entering the canopy. In the spruce forest, where the needles form active sites in the winter as well as summer, the total quantity of acid under the canopy is approximately four times greater than that in the precipitation.
2. Carbon and nitrogen stores in the soil are increasing as a result of slow breakdown of humus under the more acid conditions prevailing.
3. Reactions in the soil, particularly those involving changes in nitrogen, generate further quantities of acid. In the beech forest, the internally generated acid, together with that reaching the forest floor, is over five times greater than that in the precipitation.
4. During the period in which these ecosystems have been studied, major changes in soil chemistry have occurred involving the release of aluminum into the soil solution as a result of the reaction of the acid with the aluminum silicate in clay.

5. Necrosis of the fine roots has occurred as a result of the toxic action of inorganic aluminum salts in the mineral soil. The organically complexed aluminum in the humus layer is apparently less toxic and the fine rootlets in this upper zone allow survival of the trees in a highly stressed condition involving less foliage, dry and brittle crowns, etc.
6. The condition of the trees is such that their ultimate survival is unlikely and, at least in the case of the beech forest, seedlings will not survive because of aluminum toxicity to their roots.
7. As with agricultural soils, liming appears to be the only remedial measure to rectify the damage already done to the soil in these areas.
8. Analysis of soil cores taken from areas in which fir dieback has been observed, and which are outside the main study zone, indicate that aluminum toxicity is involved.

The possible significance of these findings to the Canadian forest is discussed. An Appendix indicates some of the reactions and mechanisms involved and refers to the techniques used.

B. INTRODUCTION

There is considerable confusion in the literature as to the actual and potential effect of acid rain on the forest ecosystem. On the one hand there have been reports of increased rate of tree growth attributed to acid rain and this no doubt results, in certain soils, from the fertilizing effects of ammonia and nitrate present in the rain. On the other hand there have also been disturbing reports of decreased growth, tree morbidity, and even tree death and these have been attributed to biogeochemical changes in the soil believed to have resulted from the acidity of rain. Such conditions might be expected to occur in areas with calcium- and magnesium-poor soils which are inadequately buffered and sensitive to acid input. Such soils, having varying degrees of sensitivity, are present in the Precambrian Shield which covers vast areas of Eastern Canada and parts of North Eastern U.S.A. Sensitive soils are also found in South Carolina and certain

other areas in the South East. Zones with similar characteristics are found in Scandinavia and other locations in Europe.

Because of the importance of continuing growth of healthy forests in these sensitive areas it is important that we increase our knowledge as to any long-term negative effects that may emerge in the future. It is particularly important to establish the time scales involved and the corrective actions that may be needed.

It is known that the quantity of available calcium and magnesium, essential nutrients for tree growth, is low in these sensitive soils (1), and that the sulfuric acid in the rain is leaching these nutrients at an accelerated rate (2). Moreover, a large portion of these tree nutrients is normally obtained by biological breakdown of tree litter and humus, and the recycle rate may be decreasing as a result of changes in microorganism communities at the lower pH of soil. This slower release of nutrients, if this in fact occurs, might be expected to slow down tree growth. These factors are now being studied in North America.

Knowledge of a further potential problem is now emerging. It has recently been established that the aluminum present in many forest clays, which consist of aluminum silicate, is now being released in the soil as a result of sulfuric acid input from rain and this may create an additional threat to the forest. Aluminum has already proved to be a problem in acid lakes. These lakes, surrounded by sensitive soils, have become acid as a result of low pH rain and have lost or are losing their fish life.

Cronin and Schofield (3) have reported that inorganic aluminum salts present in the low pH water of these lakes result in the death of fish as a result of necrosis of their gills. These investigations have established that soluble aluminum salts are present in the groundwater and springs entering these lakes.

In addition to their toxicity to fish, aluminum salts are also known to be toxic to many plants. With agricultural crops, powdered limestone is periodically added to unbuffered soils to minimize this action. In Quebec, over half-a-million tons of limestone per year are used for this purpose.

Very little is known about the effect of aluminum on North American forest ecosystems, but Dr. Bernard Ulrich has been studying this problem in Germany for many years.

I took the opportunity of a recent visit to Sweden to return by way of Germany to discuss with Dr. Ulrich the effects which he has observed and the mechanisms and techniques developed for characterizing these changes.

Dr. Ulrich is Director of the Institut für Bodenkunde und Waldernährung (Institute for Soil Sciences and Forest Nutrition) at Göttingen University and he and his associates have been making detailed measurements of atmospheric inputs and of soil properties in the Solling Plateau of West Germany since 1966. During this extensive period of measurement they have observed serious changes in the soil chemistry which are believed to be primarily related to the triggering effect of acid rain. Serious degradation of the trees in both the beech and spruce forests have occurred following these changes in soil chemistry.

In Section C, a number of the important observations that have been made are discussed. Details with regard to techniques used and the reactions found to take place in the soil are discussed in the Appendix.

C. OBSERVATIONS MADE WITH REGARD TO FOREST ECOSYSTEMS

1. The Effect of Forest Canopy on the Input of Sulfur, Hydrogen and Other Ions on the Forest Floor

The rain water which passes through the forest canopy and runs down the bark of trees is considerably more acidic than the rain itself. This results from the fact that aerosols which consist of minute particles less than about 1 μ diameter, containing sulfuric acid, calcium sulfate, etc., present in the atmosphere are deposited on the leaves and bark as the air passes through the canopy and these are washed off by the next rain. (The aerosols are responsible for the haze which gives reduced visibility in the atmosphere). In addition, gaseous sulfur dioxide is also taken up by the bark and foliage where it is oxidized to sulfuric acid and subsequently

washed off. Measurements of unobstructed rainfall, throughfall and stemflow have been made on a year round basis for over a decade in the beech and spruce forests of the Solling Plateau (500 M elevation), 40 km N.E. of Göttingen. The area is described as a densely forested area without large industry. (It is however, about 130 to 150 km east of the Essen-Dusseldorf Industrial Area). The sulfur dioxide concentration in the atmosphere is reported to be 5 to 10 $\mu\text{g}/\text{m}^3$ in the summer and 10 - 20 $\mu\text{g}/\text{m}^3$ in the winter (4). Ulrich (5) reports that annual rainfall on a 6-year period is $955 \text{ l}/\text{m}^2 \pm 217 \text{ l}$, the variation between years. Analysis of the principle ions in the rain and under the canopy during this period is shown in Table 1.

Ulrich notes that in rainfall, a portion, approximately 58%, of the anions - SO_4^{2-} , NO_3^- and Cl^- are neutralized by Na^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , in rain, this partial neutralization resulting from ammonia and dust present in the atmosphere.

Data in Table 1 show that the quantity of H^+ and other ions reaching the forest floor is substantially higher than that present in the rain which reaches the canopy. In the case of the beech forest the acidity of rainfall (as measured by the quantity of H^+ deposited) is only 58% of the total reaching the forest floor. In the spruce forest, which holds the needles in winter, the acid rain contributes only 26% of the acidity reaching the ground.

Conversion of the values reported in Table 1 from $\text{keq}/\text{ha}/\text{annum}$ to the more familiar units of $\text{kg}/\text{ha}/\text{annum}$ are shown in Table 2. In the spruce forest the quantity of sulfuric acid formed from contact with sulfur dioxide and its oxidation in the foliage is 71 $\text{kg}/\text{ha}/\text{annum}$ compared with 38.7 $\text{kg}/\text{ha}/\text{annum}$ in rain, nearly twice the quantity. Less oxidation of SO_2 occurs in the atmosphere in the winter than in summer, and the spruce needles act as collection and oxidation sites for the higher winter concentrations of SO_2 found in the atmosphere. This extra sulfuric acid, together with that deposited from the aerosol, increased the total deposition of sulfuric acid on the forest floor from 38.7 $\text{kg}/\text{ha}/\text{annum}$ in the precipitation to 150.4 $\text{kg}/\text{ha}/\text{annum}$, 3.9 times the quantity. The sulfuric

acid deposited in the spruce forest was found to be 56% of the total of the sulfuric acid plus the sulfate salts.

The weighted 6-year mean pH values of rainfall and throughfall, in comparison with that of assumed preindustrial rain, are given by Ulrich as follows:

	pH	H ⁺ input	
		keq/ha/a	relative amounts
Preindustrial rain (assumed)	5.65	0.22	1
Current rain in Solling	4.07	0.814	37
Precipitation under Beech canopy	3.79	1.39	63
Precipitation under Spruce canopy	3.38	3.09	140

For comparison, Nicholson et al (6) have recently shown values for a Scots pine forest in an area 36 km N.W. of Edinburgh "only moderately affected by air pollution". The atmospheric SO₂ concentration was reported to be 10.5 ppb (volume)* and the annual rainfall, 821 mm. Their data are as follows:

	pH	Sulfate, mg/l	
		as S	as SO ₄ ²⁻
Precipitation	4.2	1.7	5.2
Throughfall	3.7	6.4	23.0
Stemflow	3.3	16.0	49.0

It is apparent from these studies that it is important to measure throughfall on a year round basis in order to assess the acid input to a forest. The variation in values on a yearly basis from 1969 to 1976 can be seen in lines 1 to 3 of Table 3.

Since the spruce forest removes acid aerosols and sulfur dioxide from the atmosphere, it, like clouds and rain, provides an important means for atmospheric purification. Whether or not the forest will suffer as a result depends on soil characteristics. For instance, when the forest is located on a calcium-buffered soil there may be relatively little damage, at least for many years to come. However, this is not the case in soils lacking this buffering capacity, such as those

* 30µg/m³

of the Solling Plateau. In this area, Ulrich believes, "liming" of the soil is essential as an intermediate stage, prior to the elimination of the sulfur dioxide emissions at source.

Since the combining weights of calcium carbonate and sulfuric acid are essentially the same, 100 and 98 respectively, it is apparent from Table 2 that the spruce forest of the Solling Plateau would require approximately 150 kg/ha/annum of calcium carbonate (powdered limestone) to balance current inputs. Several times this amount may be needed to remedy present damage.

2. The Accumulation of Carbon and Nitrogen in the Humus of the Beech Forest

During the study period the carbon and nitrogen stores in the organic top layer of the forest floor increased as shown below (7):

	<u>Carbon & Nitrogen Stores in Humus Layer soil, kg/ha</u>	
	C	N
1966	14,500	809
1973	20,900	953
1979	22,300	1,010

This indicates that organic nitrogen is accumulating in the soil, and that less is "mineralized", i.e. converted to nitrate which thus becomes available for recycle. The nitrogen input to the area from ammonia and nitrate in rain is approximately 20 kg/ha/annum. Earlier measurements in tree growth which indicated an extra yield due to fertilization from the rain did not continue during this period when nitrogen accumulation was observed. (7)

3. The Changes in Soil Chemistry in the Beech Forest and the Resultant Effect on the Forest

When a soil which is lacking in calcium carbonate buffering, such as that in the Solling Plateau, becomes more acidic, aluminum, rather than calcium is the principal cation entering the soil solution. This results

from reaction of hydrogen ion with the aluminum silicate (of which clay is composed) to form Al^{3+} and silica. Ulrich et al (7), and Ulrich (8) observed a very rapid increase in aluminum concentration of the Equilibrium Soil Solution during the late summer of 1969, its concentration increasing from about 1.2 mg/l to 2.4 mg/l in a two month period at 10 cm depth as indicated in Fig. 1. Similar increases were observed at lower depths. At the same time the biomass of the living fine roots (less than 2 mm diameter) decreased from 2500 kg/ha in May to about 200 kg/ha in August. Inorganic aluminum salts are toxic to roots, the concentration at which this is observed being species dependent. Toxic concentrations also depend on whether nitrate or ammonium ion is being utilized by the plant for protein production. Rorison has found that the concentration of aluminum taken in by the roots is higher when nitrate is being assimilated (9).

The fine roots in the humus layer were not affected. This possibly results from the fact that the aluminum present in the upper layer is in an organically complexed form. (Baker and Schofield (10) have established that, unlike inorganic aluminum, organically complexed aluminum is essentially non-toxic to fish). Although dilute solutions of aluminum in the mineral soil are normally present in the forms of the Al^{3+} ion at a pH of 4.0, other forms including reprecipitated aluminum can exist at acid pH and this will be discussed in the Appendix.

The fine roots which have remained intact in the humus layer have been adequate to allow the trees to survive and to grow and the forest, although considerably stressed, has not yet died out. However the trees now carry less moisture and the wood is brittle. In 1970, the year following the fine rootlet problem, and apparently as a result of the lower moisture content, the trees actually shrank in diameter, in spite of some new annual ring growth, about one third of that of the previous year.

The characteristics of the soil and trees in this forest are under continuing study. In early 1969 the Al ion concentration in the soil was only 0.15 mg/l at 45 cm depth while in 1973 and 1979 the concentration was approximately 10.5 times greater.

The sudden increase in soluble aluminum in 1969 was attributed to an increase in the mineralization of nitrogen in the humus which occurred as a result of a very hot dry period. When organic nitrogen breaks down to inorganic nitrate, hydrogen ion is released and this, in turn, results in the solution of aluminum. This mineralization reaction is highly temperature dependent, and it is believed by Ulrich (7) that the continuing acidification from the atmosphere, could, when coupled with a future organic nitrogen mineralization surge, result in the death of these trees.

Regardless of this, the beech forest in the Solling is apparently doomed in the long run since it has been found that the seedlings will no longer grow in these soils because of damage to their roots (7).

4. The Effect of an Acidifying Forest Ecosystem and Fluxes and Stores of Nutrients

In an ecosystem involving an undisturbed growing forest on a well buffered soil receiving relatively unpolluted rain, the essential nutrient needs of the growing trees are supplied by a series of fluxes (flows) of water containing essential nutrients, such as nitrogen and phosphorus together with K^+ , Mg^{2+} , and Ca^{2+} . These nutrients are taken from ample stores in the soil which are maintained largely by recycling from the decomposition of humus and tree-litter from the biomass above. This decomposition results from action of bacteria, fungi and soil fauna, and equilibria are established by a complex series of feed-back mechanisms. Losses of the inorganic nutrients from this recycling system as a result of "leakage" to groundwater or otherwise are made up by mobilization from certain minerals present in the soil while inorganic nitrogen is obtained from the rain or "fixed" by bacteria in the soil.

A perturbation such as that arising from acidified rain, particularly on unbuffered soils, can modify the soil communities and trigger a whole series of undesired reactions and effects.

As previously shown, aluminum, released from clay in the soil by acid, has a negative effect on fine roots in the mineral soil with the result that less moisture enters the tree. Normally a substantial portion of the water entering the soil from rain is returned to the atmosphere by transpiration, i.e. evaporation from the foliage of the trees. A reduction in this evaporation rate increases the flow in the soil from the root zone to groundwater thus increasing the loss of K^+ , Mg^{2+} and Ca^{2+} . (11)

The retention of soluble salts in the soil, in spite of percolation of rain water, is dependent on cationic exchange properties of clay and of organic matter. (This retention can be compared with that obtained by the cationic resin in commercial water softeners). Unfortunately the cationic storage capacity of these soil constituents decreases with increasing acidity, the value at pH 3.0 being only 10% of that at pH 7.0. (11)

This leakage from the rooting zone of already scarce nutrients increases as the soil becomes increasingly more acid at lower depths. Quantities of minerals such as feldspars from which these cations can be mobilized may be relatively small in these sensitive soils and a deficiency of one or more could have a serious negative effect on growth, in the event that the trees have not already succumbed to aluminum toxicity.

In addition to the inputs of acidity from the atmosphere a number of reactions which generate or consume hydrogen ions can occur in the soil, particularly those involving transformation of nitrogen from one form to another. A discussion of some of these reactions is given in the appendix. Although generation and consumption are reasonably balanced in an equilibrium forest ecosystem, this is far from the case in the Solling beech forest.

A comparison of acid inputs from the atmosphere with those generated in the humus and mineral soils for the years 1969 to 1976 is shown in Table 3. Lines 1 to 3 cover atmospheric inputs and 4 to 6 the internally generated acidity. (7) The average value for H⁺ production in the soil was 2.56 keq/ha/annum, substantially greater than the corresponding value of 1.63 keq/ha/annum for atmospheric inputs. Considerable year to year variation is observed, but clearly the character of the forest soil is in a state of continuous degradative change.

5. The Changes in Soil Chemistry in the Spruce Forest and the Resultant Effect on the Forest

The pH and chemical concentrations in the ground water of a spruce forest in the Solling Plateau have been studied since 1973. Fig. 2(a) shows the change in pH and the aluminum content of the soil solution. (These curves have been redrawn from Fig. 10 of Ulrich's paper (8)).

The soil solution in which concentrations are measured is extracted at 90 cm depth using the porous plate lysimeter (See Appendix for description of technique). During 1973 and 1974 the pH was above 4.2 and the Al concentration averaged about 4.0 mg/l with a lowering of the concentration in the early autumn, as can be seen from Fig. 2(a). During 1975 the pH decreased to about 3.8 and the aluminum concentration rose sharply, establishing a new range averaging about 16 mg/l.

As shown in Section C-1, the acid input to the spruce forest is substantially greater than that to the beech forest and this is reflected in the higher aluminum concentrations in the soil water. Spruce is known to have a higher resistance to acid soils than hardwoods. However, at the current aluminum concentrations the spruce trees have low moisture content in the crowns. The needles are becoming relatively sparse and the tops are subject to wind damage. Ulrich believes that the continued inputs of acid, together with acid generated in the soil, will lead to excessive levels of aluminum accompanied by depletion of the already small stores of calcium and magnesium in the groundwater. If allowed to continue this will result in ultimate failure of the forest in such areas, it being replaced by heather or grass.

Ulrich's original studies fifteen years ago were intended to establish the reactions and responses in forest ecosystems, and it was only in the course of these investigations that he became fully aware of the serious threat of atmospheric inputs. It had been observed shortly after the second world war that forest fertilization could lead to important yield gains, but during the sixties disappointing results were frequently obtained. A possible reason for this can be seen from Fig. 2(b). A potassium and nitrogen fertilizer was added to spruce forest soil adjacent to the area from which the data are taken in Fig. 2(a). The addition of the fertilizer, indicated at Point A in Fig. 2(b), led to a surge of aluminum ions in the soil water (8). Realizing that the effect of the fertilizer was counter-productive, the soil was limed as indicated by Point B. This reduced the soil water aluminum concentration substantially, and the longer term effects will be observed. Obviously, fertilization, without simultaneous liming of the soil, in such areas would be counter-productive.

Ulrich believes that the liming of the soil, a technique well established for agricultural lands to counteract the deposited and internally developed acidity, and the export of nutrients with crops, will have to be practised in the forest, for similar reasons. (12).

6. The Dieback of Silver Fir in Central Europe

A serious dieback of fir (*abies alba*) is now occurring in Europe (13)(14). These forests, in Eastern Bavaria and throughout Central Europe, are outside the area which Ulrich has been examining in detail as referred to above. The exact reasons for this dieback have not yet been established by those who have been working directly with the problem. (13)(14). The symptoms, prior to death of the tree, involve lack of needles and dead "storks nest" crowns. The pathological condition begins in the roots and the lower stem which has high moisture content referred to as "wet wood" (15).

The fibres in the conductive sapwood have poor moisture conductivity properties (14). Densely woven networks of rhizomorph bacteria are found on the roots and in the soil to a depth of 1.5 m.

Ulrich has found, from preliminary examination, that soils where the dieback has been observed have characteristics similar to those of the Solling Plateau. He has postulated that accumulation of organic nitrate in the humus in cool humid years has been followed by a surge of mineralization in a warm dry year, with the characteristic release of hydrogen ions that accompanies nitrate formation. This, together with the high acid input, can lead to an aluminum concentration sufficiently high to be toxic to the roots. The damaged roots allow entrance of bacteria, causing the "wet wood", which in turn leads to a reduction in water conduction to the top of the tree. Ulrich is carrying out further investigation to establish the validity or otherwise of his hypothesis regarding the mechanism.

D. SIGNIFICANCE OF GERMAN FINDINGS FOR CANADA

The Solling forests down-wind from the principal German steel and industrial zone, have been subjected to serious acid impaction for a very long period of time. Thus the deterioration in the quality of the trees and forest soil are likely much further advanced than that likely to be found in Canada. The very serious results which Ulrich has described for these forests are closely weather-specific and site-specific in regard to atmospheric inputs, soil changes and the response of forest trees in the acidifying ecosystem. However, the techniques developed and used over many years by Ulrich's group, the nature of their observations, and the mechanisms proposed, are clearly of interest.

The use of special collection troughs for year-round throughfall measurement of acid deposition in the forest lead to their observation that the bark and foliage act as a trap for acid aerosols and also for sulfur dioxide which is subsequently oxidized and carried to the forest floor.

An astonishing result was the finding that the low concentration of sulfur dioxide in an atmosphere a considerable distance from source, can supply twice the quantity of acid obtained in the precipitation. This, together with the collected acid aerosol, can result in an amount of acid reaching the forest floor that is approximately four times greater than that present in the rain and snow above the canopy. To what extent is this happening here? The concentration of sulfate in the precipitation in Eastern Canada is normally substantially less in winter than in summer, and this is attributed to the slow oxidation rates in the atmosphere at low temperatures. Thus, SO_2 concentrations should be established in forest areas and whether it is being collected and oxidized by the trees. If this is so the resultant input, together with that of the collected aerosols, to the soil should be determined.

The quantities of the stores of humus, with its combined nitrogen content, and of organic acids and salts should be established in sensitive soil areas, so that changes, with time, and the effect on the acid status of the soil may be established.

The concentration, stores and fluxes of the various ions and exchangeable cations in soil water and soils should also be measured over a period of years in sensitive forest soil areas subject to relatively high impaction of acid. At the same time associated changes, if any, in the biomass should be observed, particularly if hydrogen ions are being generated in the soil.

Adjacent test areas should be limed to establish the ability of such treatment to counteract the various effects resulting from soil acidification.

The sensitivity of the roots of Canadian tree species to aluminum in soil solution and the effect of co-factors such as pH, nitrate and other cations should be established.

No doubt some aspects of such a programme are already under way at different locations in Canada, but integrated programmes, such as that at Göttingen are indicated. It is indeed important to establish whether, in fact, the impaction of acids in sensitive areas places the very existence of forest cover at stake, as Ulrich has found good reason to believe. If no threat is found, the assurance that will be provided is of great value. However, if the threat is real, a reduction in the time available for corrective action can be crucial.

APPENDIX1. Soil Reactions Involving a Change in the H^+ Status of Soil Solution

A very complex series of biogeochemical reactions are involved in the recycle and uptake of nutrients by the trees in forest soils. In general each of these reactions involve either the production or consumption of hydrogen ions. A key nutrient is nitrogen since it is required for production of the protein in DNA needed for cell replication in the growing tree.

Nitrogen enters the forest soil as NH_4^+ and NO_3^- in precipitation and in the aerosols captured by the canopy. Approximately 60 kg/ha/annum are needed for tree growth. From Table 1 it can be seen that the quantities of NH_4^+ and NO_3^- reaching the forest floor in the beech forest are 1.01 and 1.15, a total of 2.16 keq/ha/annum. The equivalent weight of nitrogen is 14 and therefore the total quantity of NH_4^+ and NO_3^- received from the atmosphere is $14 \times 2.16 = 30.2$ kg/ha/annum, about half of that needed for normal tree growth.

As pointed out in Section C-2, the store of organic nitrogen in the humus layer of this forest is 1010 kg/ha/annum, 16 times the amount needed in a year and 32 times the amount of input from the atmosphere. Thus partial decomposition of this humus is essential for adequate nitrogen recycle.

Storage of NO_3^- in the soil is very small and unless it is assimilated by the biomass at about the rate it enters the soil it "leaks" from the root zone of the tree by percolation or is "denitrified", i.e. converted to N_2 or NO_2 by bacterial action.

NH_4^+ is assimilated by the biomass either directly or by an initial "nitrification", i.e. conversion to NO_3^- which then is assimilated or lost from the system.

NH_4^+ is oxidized to NO_3^- by the action of autotrophic or heterotrophic soil bacteria (16) with the liberation of 2 hydrogen ions as indicated in the following reaction, $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$

When NO_3^- is assimilated by the roots it has been established that one H^+ is consumed. Thus assimilation of nitrate by the biomass results in a reduction in acidity. However assimilation of NH_4^+ either directly or after nitrification, involves a net increase in acidity of the soil solution.

NH_4^+ is stored in the soil to a limited extent by cationic exchange. Quantities entering the soil in excess of this storage capacity either react as indicated above or "leak" from the root zone.

The nature of these nitrogen conversion reactions is as follows:

1. Nitrification ($\text{NH}_4^+ \rightarrow \text{NO}_3^-$) H^+ released
2. Assimilation ($\text{NO}_3^- \rightarrow \text{Organic N}$) H^+ consumed
3. Mineralization ($\text{Organic N} \rightarrow \text{NO}_3^-$) H^+ released
4. Denitrification ($\text{NO}_3^- \rightarrow \text{N}_2, \text{NO}_2$ etc) H^+ consumed

Reactions 1, 3 and 4 are brought about by bacteria, fungi or soil fauna, populations and activity of which are pH and temperature dependent. (If one organism species dies out because of change in pH another organism species normally develops and takes over, but the reactions are not necessarily at the same rate).

Reaction 2 depends on the rate at which the biomass grows, and the availability of NH_4^+ and/or NO_3^- in the soil.

18.

The inorganic nutrients, Ca^{2+} , Mg^{2+} and K^+ are involved in maintaining the pH status of the tree, neutralizing uronic acids, forming such products, in the case of magnesium, as chlorophyll etc. Organic acids such as succinic, lactic and oxalic acids are also formed in the humus, increasing the acidity, but these eventually break down in the soil to form water and CO_2 , the latter being largely lost to the atmosphere, thus decreasing acidity.

A small portion of the humus is converted to the relatively stable humic acids which leave the forest soil in surface run-off, partially neutralized by calcium or sodium.

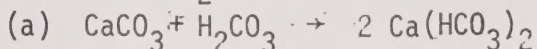
Ulrich found that in every year since 1969, an excess of H^+ is being generated in the forest soil thus further exacerbating the acidifying effect of the acid rain (7). As noted in Section C-3, Ulrich attributed the higher than average H^+ generation in 1969, as shown in line 6 of Table 3, to the very hot dry summer which resulted in mineralization proceeding at higher than normal rate. The following year the reduced tree growth resulted in reduced assimilation of NO_3^- and therefore less H^+ consumed, this in turn resulting in a higher than normal net production of H^+ .

Although Ulrich was dealing with a mature forest it follows that in periods following harvesting sensitive soils subject to high impaction of acid might be expected to acidify at an accelerating rate. The higher soil temperatures without shade could result in increased production of nitrate, without the counterbalancing neutralizing effect of assimilation of NO_3^- . Because of lack of biomass, denitrification and/or leakage through percolation of NO_3^- would follow.

2. Increasing Soil Acidity and the Dissolution of Mineral Ions from the Soil

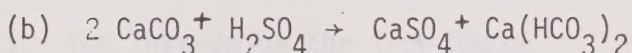
Ulrich (5) has described the reactions which occur between acid and the mineral content of soils in different pH ranges.

pH 6.5 to 8.3. Soils in this pH range are buffered with calcium and magnesium carbonate. Carbonic acid, the weak acid produced in "normal" rain from CO_2 in the air, reacts with CaCO_3 as follows:

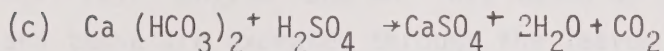


Considerable quantities of carbonic acid are also formed in the soil by root respiration and by decomposition of humus. The soluble $\text{Ca}(\text{HCO}_3)_2$, together with the slightly soluble MgCO_3 leached from the soil is largely responsible for the "hardness" of natural waters.

Sulfuric acid, the strong acid present in acid rain reacts with CaCO_3 as follows:

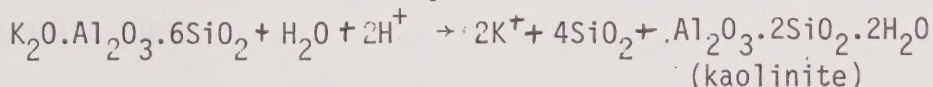


When stores of calcium carbonate are relatively small sulfuric acid will further react with calcium bicarbonate as follows:



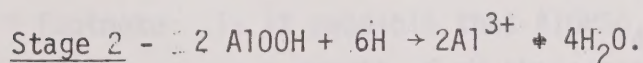
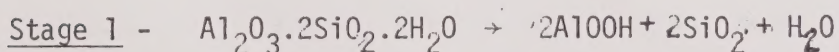
As long as there is sufficient calcium carbonate in the soil to react with all the sulfuric acid the pH will remain above about 6.5

pH 5.0 to 6.5. In soils which are essentially free of CaCO_3 the presence of feldspars will provide a second buffering range. Examples of feldspars are orthoclase, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. These react with H^+ in the following manner:



The above reaction will proceed with carbonic acid, sulfuric acid or nitric acid and allow the mobilization of the K^+ , Mg^{2+} , Ca^{2+} needed as nutrients.

pH 3.0 to 5.0. Kaolinite reacts with strong acids such as sulfuric and nitric acids but not with the weaker carbonic acid to form Al^{3+} and SiO_2 . This reaction can be shown as proceeding in two stages.



Al^{3+} is not a tree nutrient and its mobilization at low pH can have a toxic effect on tree roots as has been shown.

Although aluminum is largely in the form of Al^{3+} in dilute soil solutions at pH 4.0 or less, other forms are present in the range of 4.0 to 7.0. These include the polynuclear species $\text{Al}_7(\text{OH})_{17}^{4+}$ and $\text{Al}_{13}(\text{OH})_{34}^{5+}$ (17). It also forms a solid phase compound Al OH SO_4 (7).^{*} In addition, it is present in an organically complexed state in the humus layer.

3. Ion Take-Up by the Tree Roots

The tree roots are selective in their uptake of ions from the soil (5). Only K^+ and Mn^{2+} are taken up in greater quantity than required and these are excreted through the leaves and recycled when washed off by the rain. Sulfur, sodium, chloride and aluminum are selectively excluded by the roots, with aluminum excluded to the greatest extent and sulfur the least.

Thus when the cations are dissolved from the soil, surplus quantities over those required for the growing biomass and those held by cationic change become washed from the rooting zone at times of high hydraulic flow.

4. Methods of Sampling Used in Measurement of Ionic Balances

a) Equilibrium Soil Solution. A specialized method is used for removing the actual groundwater from the soil at different depths below the forest floor. The extraction device consists of a porous disc of approximately 25 cm diameter, one side of which is sealed to a sturdy plastic receiver having a grooved grid adjacent to the plate, these grooves leading to

^{*} Footnote: Is it possible that AlOHSO_4 precipitates in the fine roots as a result of pH change associated with NO_3^- uptake?

two small outlet nipples connected to small diameter plastic tubes. The soil solution can be drawn through these to sample bottles maintained under vacuum which are conveniently located above ground. Only one of these tubes is used at a time, the other acting as a spare. In order to place these porous plates, a small pit with vertical walls to provide working space is dug in the forest floor. Horizontal slots are cut into the side at predetermined depths into which a collector with the attached tubes is placed, porous side up. The slot is then filled with the original soil, packing it under the collector. Finally, after setting plates at different levels the pit is filled and the bottles set and evacuated. Samples are collected on a weekly basis.

As an alternative collection method, they use porous thimbles, 20 mm in diameter and 50 mm length attached at the open end to a rigid plastic tube of 22 mm diameter, with an internal small tube for withdrawing the solution connected to the thimble. Special care is needed for drilling the soil and placing the device to ensure a tight fit, and several are needed to obtain an adequate quantity of solution for each depth and site.

b) The Equilibrium Soil Solution. This is obtained by extracting with water samples of soil obtained with a core borer. The moisture content of the soil is first established and then a separate fresh sample is extracted after 24 hours contact of soil and water, the ratio being 80 g total water to 100 g soil, moisture-free basis. The sample is stirred in the presence of the water and the solution removed by centrifuging. Analyses are carried out on this solution.

5. The Cation Exchange Capacity

A 20 g soil sample is mixed with 1 n NH_4Cl on a special sintered filter device and allowed to stand for 3-4 hours. The ions are then leached from the soil by passing a total of 100 ml of the NH_4Cl solution through the filter. This releases the various ions

from cationic exchange sites and allows the determination of the ratio of the various ions in which they were held in the soil.

6. Appendix Summary

Dr. Ulrich and his associates have developed and perfected techniques for measuring through-fall, stem-flow and soil solutions and properties at different depths beneath the forest floor. The analytical data obtained in this way have given important insights into the changes and mechanisms involved in the soil and the negative effects which have been observed in highly stressed forests in Germany.

It is believed that similar studies should be incorporated into forestry research in Canada.

BIBLIOGRAPHY

1. Weetman, G.F., and Webber, B., "The Influence of Harvesting on the Nutrient Status of Two Spruce Stands", *Can. Jour. For. Res.* 2, 351-369, 1972.
2. Dillon, P.J., Jeffries, W.A., Scheider, W.A., and Yan, N.D., "Some Aspects of Acidification in Southern Ontario", pp 212-213 in "Ecological Impact of Acid Precipitation", Sandefjord Conference, Drablos, D. and Tollan, A., Editors, SNSF Project Oslo-As, 1980.
3. Cronin, C.S., and Shofield, C.L., "Aluminum Leaching Response to Acid Precipitation: Effects on High Elevation Watersheds in the Northeast", *Science* 204, 304-305, 1979.
4. Mayer, R. and Ulrich, B., "Input of Atmospheric Sulfur by Dry and Wet Deposition to Two Central European Forest Ecosystems", *Atmospheric Environment*, 12, 375-377, 1978, Pergamon Press.
5. Ulrich, B., "Production and Consumption of Hydrogen Ions in the Ecosphere", Chapter in "Effects of Acid Precipitation on Terrestrial Ecosystems", Hutchinson and Havas, University of Toronto, NATO Conference Series, pp. 255-282.
6. Nicholson, I.A., Cape, N., Fowler, D., Kimmand, J.W., and Paterson, I.S., "Effects of Scots Pine Canopy on the Chemical Composition and Deposition Pattern of Precipitation", pp 148-149 in "Ecological Input of Acid Precipitation", Sandefjord Conference, Drablos, D., and Tollan, A., Editors, SNSF Project Oslo-As, 1980.
7. Ulrich, R., Mayer, R., and Khanna, P.K., "Chemical Changes Due to Acid Precipitation in a Loss Derived Soil in Central Europe", *Soil Science*, 130, pp 193-199, 1980.
8. Ulrich, B., "Die Wälder in Mitteleuropa: Messergebnisse ihrer Umweltbelastung, Theorie ihrer Gefährdung Prognose ihrer Entwicklung", *Sondendruck aus Allgemeine Forst Zeitschrift*, Nr 44/80, Lothstrasse 29, 8000 München 40.
9. Rorison, I.H., "The Effect of Soil Acidity on Nutrient Availability and Plant Response", Chapter in "Effects of Acid Precipitation on Terrestrial Ecosystems", Hutchinson and Havas, University of Toronto, NATO Conference, Series pp 283-303.
10. Baker, J.B., and Schofield, C.L., "Aluminum Toxicity to Fish as Related to Acid Precipitation and Adirondack Surface Water Quality", pp 292-293 in "Ecological Impact of Acid Precipitation", Drablos, D. and Tollan, A., Editors, Sandefjord Conference, SNSF Project Oslo-As 1980.
11. Ulrich, B., . . . A systems Approach to the Role of Nutrients in Controlling Rehabilitation of Terrestrial Ecosystems. NATO Conference Series 3. Break-down Restoration Ecosystem pp 105-121 (1978).
12. Reference (5) p. 278.
13. Schuck, . . . H.J., Bldmel, U., Geier, I., and Schütt, "Schadbild und Atiologie des Tannensterbens", *Eur. J. For. Path.*, 10, 125-135, 1979.
14. Bauch, J., Klein, P., Frühwald, A., and Brill, H., "Alterations of Wood Characteristics in *Abies Alba* Mill. due to "fir-dying" and Considerations Concerning its Origin", *Eur. J. For. Path.* 9, 321-331, 1979.
15. Ulrich, B., "Eine Okosystemare Hypothese über die Ursachen des Tannensterben", Paper for Publication, Göttingen University, 1981.

16. Alexander, M., "Effects of Acid Precipitation on Biochemical activities in Soil", pp 47-51, in "Ecological Impact of Acid Precipitation, Sandefjord Conference, Drablos, D. and Tollan, A., Editors, SNSF Project Oslo-AS, 1980.
17. Nair, V. D. and Prenzel, J., "Calculations of Mono- and Polynuclear Hydroxyaluminum Species at Different pH and Total Aluminum Concentrations." Z. Pflanzenernaehr, Bodenkd, 141, 741-751 (1978).

TABLE 1* DEPOSITION OF IONS IN RAIN AND TRAPPED BY TREES IN BEECH AND SPRUCE FOREST IN SOLLING PLATEAU, GERMANY - 6-YEAR AVERAGE

	Values keq/ha/annum (unless shown as %)									
	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Mn ²⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
<u>SPRUCE FOREST</u>										
Rain and snow input	0.79	0.35	0.78	0.09	0.55	0.17	0.01	0.51	0.48	1.44
Trapped by trees	2.28	0.43	0.23	0.23	1.18	0.25	0.05	0.64	0.48	4.04
Total under canopy	3.07	0.78	1.01	0.32	1.73	0.42	0.06	1.15	0.96	5.48
Precipitation as % to Forest Floor	26%	45%	77%	28%	32%	40%	17%	44%	50%	26%
<u>BEECH FOREST</u>										
Rain and snow input	0.79	0.35	0.78	0.09	0.55	0.17	0.01	0.51	0.48	1.44
Trapped by trees	0.58	0.30	0	0.16	0.78	0.19	0.04	0.45	0.16	1.83
Total under canopy	1.37	0.65	0.78	0.25	1.33	0.36	0.05	0.96	0.64	3.27
Precipitation as % to Forest Floor	58%	54%	-	36%	41%	47%	20%	53%	75%	44%

* Table assembled from Tables 4 and 5 of Reference 5

TABLE 2

QUANTITIES OF SULFURIC ACID AND SULFATE DEPOSITED
IN THE SOLLING PLATEAU ECOSYSTEMS

	Total Acidity Deposited		Total Sulfate Deposited		Acidity % of Total Sulfate
	H ⁺ keq/ha/a	as H ₂ SO ₄ kg/ha/a	SO ₄ ²⁺ keq/ha/a	as H ₂ SO ₄ hg/ha/a	
<u>SPRUCE FOREST</u>					
From precipitation only	0.79	38.7	1.44	70.6	55
From oxidation of SO ₂ in trees	1.45	71.0	1.45	71.0	100
From deposition of aerosols	0.83	40.7	2.59	126.9	32
Total from SO ₂ and aerosols	2.28	111.7	4.04	197.0	57
Total reaching forest floor	3.07	150.4	5.48	268.0	56
<u>BEECH FOREST</u>					
From precipitation only	0.79	38.7	1.44	70.6	55
Total from SO ₂ and aerosols	0.58	28.4	1.83	89.7	31.6
Total reaching forest floor	1.37	67.1	3.27	160.2	41.9

TABLE 3 ANNUAL VALUES OF H⁺ INPUT TO FOREST FLOOR AND NET H⁺ GENERATED IN SOIL IN BEECH FOREST IN SOLLING PLATEAU*

	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>Average</u>
<u>H⁺ Input to Forest Floor</u>									
1. Input in Precipitation	0.69	1.10	0.71	0.92	1.00	0.66	0.83	0.61	0.82
2. Trapped in Canopy	0.94	0.93	0.58	0.78	0.80	0.92	0.86	0.67	0.81
3. Total Input (1 and 2)	1.63	2.03	1.29	1.70	1.80	1.58	1.69	1.28	1.63
<u>Net H⁺ Generated Internally in Soil</u>									
4. Generated in humus	1.1	1.4	0.9	0.7	0.6	0.9	0.5	0.7	0.85
5. Generated in Mineral soil	2.3	2.1	0.7	1.4	1.8	1.7	2.6	1.4	1.75
6. Total Generated (4 and 5)	3.4	3.5	1.6	2.1	2.4	2.6	3.1	2.1	2.60
7. Total of 3 and 6	5.0	5.5	2.9	3.8	4.2	4.2	4.8	3.3	4.2

*Table assembled from Tables 3 and 4 of reference (7).

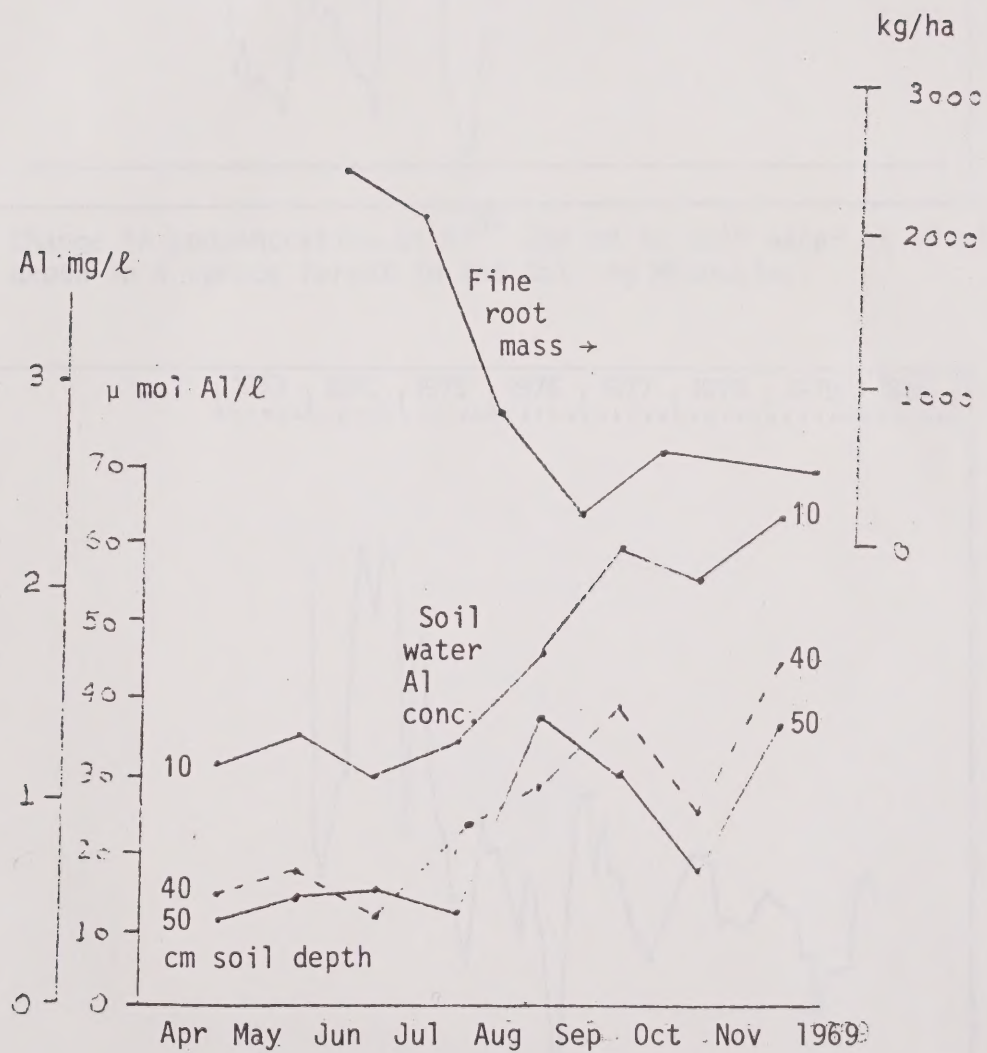


FIG. 1. Changes in aluminum concentration in soil solution and fine root mass in a beech forest at Solling, Germany

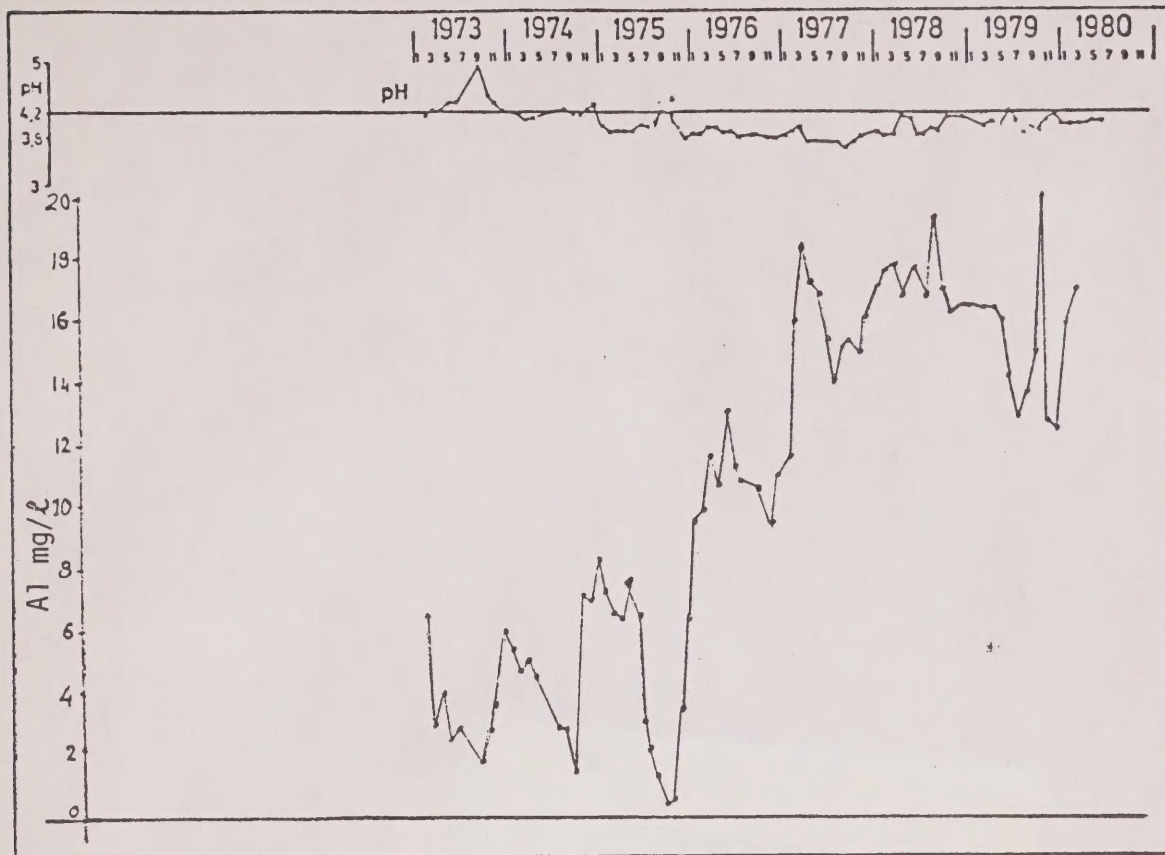


FIG. 2(a). Change in concentration of Al^{3+} and pH in soil water at 90 cm depth in a spruce forest in the Solling Mountains

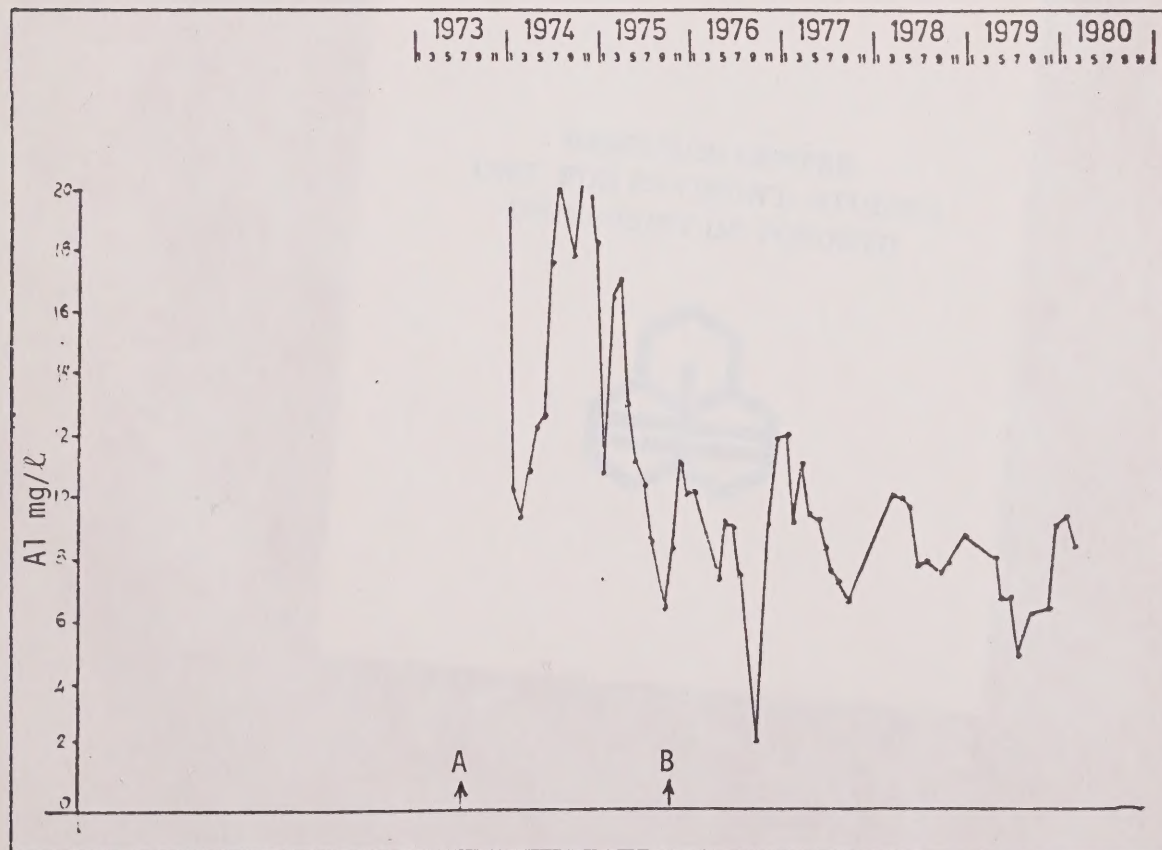


FIG. 2(b). Al^{3+} in soil water in a spruce forest area immediately adjacent to that shown in Fig. 1(a), illustrating the effect of addition of potassium and nitrogen fertilizer at A and calcium carbonate at B.

CA7 DT 81A16 A16

Dontar

ACID RAIN AND THE FOREST: THE EFFECT OF ALUMI
THE GERMAN EXPERIENCE. / Tomlinson, G.H. 1981

RESOURCE CENTRE
INST. FOR ENVIRON'L. STUDIES
UNIVERSITY OF TORONTO



